Determination of the mechanical properties of gelatinized starch granule from bulk suspension characterization

Arnesh Palanisamy, Gabrielle Moulin, Marco Ramaioli, Artemio Plana-Fattori, Denis Flick, Paul Menut

Determination of the mechanical properties of gelatinized starch granule from bulk suspension characterization

Arnesh Palanisamy[a], Gabrielle Moulin[a], Marco Ramaioli[a], Artemio Plana-Fattori[a], Denis Flick[a], Paul Menut[a,*]

[a] *Université Paris Saclay, INRAE, AgroParisTech, UMR SayFood, 91300, Massy, France*

Abstract

Gelatinized starch granules are soft and deformable particles that are commonly used in food products as texture modifiers. Modelling the flow behaviour of such suspensions during industrial processes requires the knowledge of the mechanical properties of the swollen granules, however, such data is usually lacking because of the difficulties inherent to the determination of mechanical properties of particles that are heterogeneous in terms of size and shape. We investigate here the rheological properties of dense suspensions prepared at different volume fractions and by different means (centrifugation, limited water swelling, osmotic compression) to estimate the mechanical properties of an "averaged" starch granule. Results show that starch granule exhibits a rough surface and behave as frictional particles. We compare the shear modulus value determined assuming either frictionless (previous model) or frictional interactions (as suggested by our results), the latter giving shear modulus lower by about one order of magnitude. This study also allows the first estimate of the starch granule bulk modulus, which value is corresponding to a Poisson ratio of 0.47, close to the maximum value of 0.5. The swollen granule shear modulus is also shown to be temperature independent in the range commonly found in industrial processes (20-90 °C). These results pave the way towards multiscale mechanistic modelling of the flow of starch suspensions, to derive macroscopic rheological properties from the description of the microscopic granule properties.

Keywords: Microgel, Shear modulus, Bulk modulus, Thermal effects, Particle Elasticity

1. Introduction

In its native form, starch is found as dense granules in a variety of grains and tubers. After industrial fractionation and in some cases, chemical/thermal treatments, a large variety of starch granules with contrasted properties are obtained. These starch granules that differ in terms of textural properties, or stability against mechanical, Physico-chemical or thermal stresses, are produced for various specific applications such as enhanced oil recovery in oil drilling applications or thickening agents in food products (Ratnayake and Jackson, 2008; Nawaz et al., 2020). Global starch production is expected to reach around 156 metric tonnes by 2025 (Reportlinker.com, 2020), of this roughly 60% is used for food-based applications and 40% is expected to be used for industrial uses including oil, pharmaceutical, paper, etc.

Thermal treatments are commonly used in food processing and are usually applied to products that are highly hydrated. Applying a thermal treatment to native starch granules in the presence of excess water results in important modifications of their properties. In their native state, starch granules are solid particles, more or less spherical, in which starch macromolecules (amylopectin and amylose) are densely packed so that these granules only have a very limited water absorption capacity. However, if the temperature exceeded $\sim 70°C$, an important swelling of the particles is very rapidly observed if water is available around the granule. The influx of water is driven by the enthalpic interactions between the hydrogen bonding sites of starch and water (Renzetti et al., 2021). This process, during which the particle can absorb more than 10 times its mass in water, is called gelatinization. During gelatinization, the volume fraction of the starch particles present in a starch suspension strongly increases, and so does the suspension viscosity.

If the volume fraction of the particles in solution remains very low, i.e. much below the random close packing volume fraction ϕ_{rcp}, that is the maximum volume fraction that can be reached by solid undeformable particles packed randomly, it behaves as a hard particle suspension at low shear rates (Einstein, 1905; Batchelor, 1977). However, at high enough starch volume fractions, these suspensions form thick pastes (gelatinization is also called

*corresponding author
Email address: paul.menut@agroparistech.fr (Paul Menut)

starch pasting(Chen et al., 2007)) which exhibit properties that are similar to the ones of dense suspensions of soft microgel particles, with both solid-like and fluid-like properties(Seth et al., 2006). At low stresses, they behave like elastic solids and deform reversibly under stress. However, once sufficient stress is reached they begin to flow and show the properties of a fluid. The threshold stress at which they begin to flow is called the yield point. Soft particle pastes have a jammed amorphous microstructure that is the source of their rheological behaviour. At volume fractions higher than ϕ_{rcp}, soft particles start to deform to accommodate more neighbouring particles (Menut et al., 2012; de Aguiar et al., 2018). Further compression results in particle shrinkage. Therefore, their volume fraction, also called packing fraction, that is estimated from the volume occupied by the particles in the diluted state, can exceed 1 (Seth et al., 2006; Evans and Lips, 1992).

With the advent of particle-based simulation methods, such as Discrete Element Modelling and CFD-DEM, there is significant interest in developing simple methods to characterize material properties such as particle Young's modulus and Poisson's ratio, required as a model input. One of the most common contact models used for simulating particles is the Hertzian contact model. This model takes into account the curvature of the spherical surfaces while predicting the interaction forces on the colliding particles. According to this contact model, a repulsive force exists when the granules overlap and no force exists when they do not overlap (Di Renzo and Di Maio, 2005). To predict these normal and tangential repulsive forces one needs two parameters namely, Young's modulus and Poisson's ratio. To fully describe suspensions behaviour, lubrication forces need to be integrated, they arise due to the presence of the fluid layers in between particles. The momentum of a granule is imparted to the surrounding fluid and subsequently the other granules, hence leading to transport of momentum, even when granules are not physically in contact with each other. One requires interstitial fluid viscosity, surface roughness, position and velocities of particles for predicting the lubrication forces. For homogeneous isotropic materials, simple relations exist between the three elastic constants are Young's modulus, the bulk modulus and the shear modulus. These relations allow calculating them all as long as two are known, as they are related by the following equations.

$$K = \frac{E}{3(1-2\nu)} \tag{1}$$

$$G = \frac{E}{2(1+\nu)} \tag{2}$$

where K, G, E and ν are respectively the bulk modulus, shear modulus, Young's modulus and Poisson's ratio. These relations could be applied to describe the whole behaviour of dense suspensions, which at a macroscopic scale could be considered homogeneous and isotropic. Individual starch granules, however, are non-spherical particles, and their individual behaviour might deviate significantly from one of the homogeneous and isotropic particles. Therefore a strategy could be to determine only "averaged" properties, as it is usually done for example for their size determination, done by static light scattering assuming a spherical shape.

Techniques at the particle level exists for deciphering materials properties of individual particle material properties in literature (Villone et al., 2019; Villone and Stone, 2020; Abate et al., 2012; Mohapatra et al., 2017). Typical techniques include atomic force microscopy(AFM) based on nano-indentation, Brillouin light scattering(BLS), microfluidics, tensionmeter. In AFM based techniques a Poisson ratio is assumed and the Young's modulus is deducted from resisting force vs displacement data (Kaufman et al., 2017; Aufderhorst-Roberts et al., 2018). However, these techniques are not straightforward to apply to measure a particle averaged modulus for such a complex system of soft particles with a very high degree of variability in terms of size and shapes. BLS data is used to infer the Poisson's ratio (Mohapatra et al., 2017). In microfluidic approaches, a particle is compressed through a tapered channel and as pressure is developed by increasing the flow rate, the particle deforms due to the pressure and penetrates further into the channel. The penetration depth is optically observed and Young's modulus is deduced (Villone et al., 2019). Similarly, tensiometer and microgel based techniques make use of surface tension to generate force for deformation and optical techniques for measuring the deformation (Abate et al., 2012; Villone and Stone, 2020). However, the applicability of these techniques is not straightforward for non-spherical, poly-disperse, complex suspensions such as starch suspensions. Typical DEM models make the spherical particle assumption, albeit the 'multi-sphere' approach and methods for specific shapes such as super-quadratics exists (Lane et al., 2010; Preece et al., 1999). For non-spherical particles with no particular shape features, it is a standard practice to simulate spherical particles with averaged particle properties. One simple methodology to obtain such average particle properties is to infer them from the bulk response of the dense suspensions, which behave macroscopically as homogeneous isotropic materials, and then to determine from that an "averaged" properties at the level of the individual particles. Such use of average 'calibration techniques' are also a common feature in powder and dry granular material simulations using DEM (He et al., 2015; Yan et al., 2016; Orefice and Khinast, 2020). This approach is also useful in 'coarse-graining' simulations where the actual system is too large and one simulates at a mesoscale with larger 'representative particles' instead of actual particle sizes to reduce the computational costs.

In this article, the average mechanical properties of a large population of starch granules are investigated from bulk rheological measurements conducted on dense suspensions. To estimate the average particle shear modulus, the suspension shear modulus was measured . Two extreme hypothesis were considered, namely the fully frictional and the friction-less scenarios, to determine an upper and a lower limit for the particle shear modulus. The likelihood of the two assumptions is critically discussed. Then, we investigate the particles bulk modulus by osmotic compression. Finally, we investigate how particles shear modulus depend on the temperature, in the range 20-90°C.

2. Materials and methods

Chemically cross-linked waxy maize starch (C*Tex 06205), provided by Cargil (Baupte, France) was used for the entire study. Waxy maize starch contains more than 99 % amylopectin, and chemical cross-linking prevents the release of macromolecules during gelatinization.

2.1. True density measurement

The starch particles true density was measured using an air pycnometer (micromeritics AccuPyc 1330). We determined a true density $\rho_{true,starch}$ = 1.321 +/- 0.002 g/ml (average value from 6 repeats).

2.2. Centrifugation

In a 2-litre mixing vessel, we introduced 15 grams of starch before the addition of 1 litre of distilled water. The mixture was heated to 90 °C while mixing a 50 rpm using an IKA eurostar 60 mixer with a 3 blade propeller of diameter 5 cm; and held at this temperature for 15 minutes to ensure complete swelling of the starch granules. After letting the suspension cool down to room temperature, it was transferred into centrifuge tubes and centrifuged (SIGMA 3-18KS centrifuge) in the required conditions of rotation speed and duration. The supernatant (excess water layer) was carefully removed and the pellet, which consisted of densely packed swollen starch granules, was recovered for rheological characterization and dry weight measurements to estimate the volume fraction. A combination of centrifugation speeds ranging from 500g to 10000g and centrifugation duration ranging from 15 minutes to 30 minutes resulted in swollen starch suspensions with volume fractions ϕ ranging from 0.447 to 0.552.

2.3. Osmotic compression

22.5 grams of starch were added to 1.5 l of distilled water in a mixing vessel. The mixture was gelatinized at 90 °C as described previously (2.2). After letting the suspension cool down to room temperature, it was transferred into a regenerated cellulose dialysis tube with a cut-off of 6-8 kDa (spectra/por 1, diameter 40 mm). The dialysis tube was clipped at both ends and placed for osmotic compression inside a solution of Poly-Ethylene Glycol (PEG, $20kg.mol^{-1}$) of known concentration. After osmotic compression, the compressed samples were recovered and subjected to rheological characterization and dry weight measurements to estimate their volume fraction. We used PEG 20kDa concentrations ranging from 0.2% to 5% (wt/wt) and compression times ranging from 2 to 15 days to produce samples with volume fractions ϕ ranging from 0.46 to 1.69.

For the estimation of bulk modulus, we used the same protocol as described above, however, to ensure a constant osmotic pressure (that could decrease with time due to water diffusion from the sample to the PEG bath), the PEG bath was renewed 3 times. To determine the osmotic pressure corresponding to a given PEG concentration, we used the phenomenological one-parameter equation of state proposed by Cohen et al. (2009), which correctly described the behaviour of PEG (and others neutral flexible polymers in good solvents). This equation, based on the sum of a van 't Hoff and a des Cloizeaux terms, include a fitted parameter α, also called the "crossover index", which is polymer size-dependent and for which we used the value proposed by Li et al. (2015) for PEG 20kDa. In that case, the osmotic compression lasted around 17 days to ensure equilibrium without any degradation or granule softening.

2.4. Limited water swelling

After the addition of a known quantity of starch (ranging from 5 to 25 grams) into 100ml of water in a mixing vessel, the suspension was heated up to 90 °C and held at this temperature for 15 min under constant mixing. The sample was then cooled down to room temperature and recovered for rheological characterization and dry weight measurements. This resulted in starch suspension with volume fractions ϕ ranging from 0.42 to 1.90.

2.5. Dry weight measurement and volume fraction determination

Dry weight measurements were conducted at 100 °C in an oven (Chopin technologies). Prior measurements showed that after 24h at 100 °C the sample had reached a constant weight, therefore all samples were let in the oven for 24h before dry weight measurement. Samples were introduced in an aluminium foil previously weighted, and the weight of the sample was determined before (M_1) and after (M_2) drying so that the sample dry starch content could be determined as $S_{dry} = M_2/M_1$. Therefore, the starch concentration in the suspension, C_s (in g of starch per 100g of water) is given by $C_s = 100 * \frac{S_{dry}}{1-S_{dry}}$

The corresponding equivalent volume fraction of unswollen starch granules, ϕ_{ug} , is given by

$$\phi_{ug} = \frac{C_s}{\rho_{true,starch}} * \frac{1}{100 + \frac{C_s}{\rho_{true,starch}}} \tag{3}$$

With $\rho_{true,starch}$ the true density of unswollen starch previously determined assuming density for water $\rho_{\text{water}} = 1000\ kg/m^3$.

To estimate the volume fraction of swollen granules, we used data from previous microscopic experiments showing that, on average, the starch granule radius (the geometric mean of the Feret diameters) increases 2.35 times when gelatinized in excess of water (Palanisamy et al., 2020; Deslandes et al., 2019). Thus, assuming that the granules are spherical and the total volume is conserved (volume gained by the starch during swelling is lost by water), one can estimate the volume of the swollen starch granules divided by the volume of the suspension: ϕ, which is also known as the volume fraction. Please note that based on the definition here volume fraction is notional and thus can exceed 1. Similar definitions have been used extensively in the literature for various other suspensions as well (Mattsson et al., 2009).

$$\phi = (2.35^3) * \phi_{ug} \tag{4}$$

2.6. Rheology

The rheological measurements were all performed in a Couette cell using an Anton Paar MCR92 rheometer. The characterization of the dense suspensions of swollen starch granules was performed at 20 °C. The mechanical properties were first probed at constant frequency (f = 1 Hz) and strain (γ= 0.01) for 120 seconds, with an acquisition rate of 1 point per second. Then, a frequency sweep was carried out at constant strain γ= 0.01, from f = 0.02 Hz to f= 3.5 Hz. Storage modulus obtained from single point measurements are plotted in figure 1. The frequency and loading effects were negligible compared to the volume effects.

The effect of temperature on the rheological properties was also evaluated. A rejuvenation and ageing step was performed prior to the first measurement, in order to limit measurements error resulting from the sample history (Cloitre et al. (2000)). Rejuvenation consists of shearing the sample at shear stress greater than the yield stress thus allowing the flow of the sample. Here, the sample was sheared at a shear rate $\dot{\gamma} = 50\ s^{-1}$. The following ageing step consists in holding the sample at rest for 45 minutes. Sedimentation experiments showed the absence of settling in the sample during all the duration of the experiments, which can be attributed to the large volume fraction of the samples (above random loose packing), combined with a low density difference between the swollen starch granules and the surrounding water. Rheological properties were measured at 20 °C; 40 °C, 60 °C, 80 °C and finally 90 °C, the ramp rate during heating being 2 °C per minute. At each temperature, the rheological properties were measured at constant frequency $f = 1$ Hz and constant strain $\gamma = 0.01$ for 120 seconds with an acquisition rate of 1 point per second. For cooling the sample from 90 °C to 20 °C, a ramp rate of 0.4 °C per minute was used, and sample properties were again measured once thermal equilibrium was reached.

2.7. Confocal laser scanning microscopy

Gelatinized samples obtained by the limited water swelling method and characterized by a particle volume fraction close to 0.4 were observed using a confocal laser scanning microscope (CLSM) (Leica TCS SP8, Germany). 0.5 ml of starch solution was stained using 50 μL of Congo Red solution (1% in water, Sigma-Aldrich). Two 250 μm thick spacers were used to place the stained solutions on the microscope slides. The solutions were excited with a laser at 488 nm and the emitted fluorescence was detected in the range 497 - 717 nm. The laser was used at 85% of the maximum intensity. Samples were observed with a 40X water objective. The total number of pixels in each picture is 3224 x 3224 and each pixel correspond to 0.09 μm. Thus, the length and width of each picture corresponds to 290.62 μm. A total of 192 scans were performed using 0.422 μm step for a total sample height of 80.67 μm to generate a stack of images. Each of these 192 images was manually analyzed to count the number of neighbours of some representative granules.

2.8. *Bulk modulus measurements through osmotic compression*

To measure the bulk modulus of the suspension using osmotic compression, one first needs to establish the time taken for the sample to equilibrate osmotically with the surrounding medium. To do so, we followed the dry weight evolution during osmotic compression, at two different PEG concentrations, and determined the corresponding volume fraction (Table 1). After 17 days, the volume fraction tend to reach a plateau. Above 17 days, the increase in volume fraction is very limited, but we observed by rheology a decrease in the sample shear modulus, that could result from starch degradation and granule softening, thus only samples obtained after 17 days will be considered for analysis.

time [days]	ϕ-3% PEG20K [wt/wt]	ϕ-4% PEG20K [wt/wt]
4	0.76	0.99
9	1.20	1.60
14	1.39	1.67
17	1.45	1.69
21	1.46	1.75
24	1.47	1.75

Table 1: Evolution of the sample volume fraction during osmotic compression, at two different PEG concentrations

3. Results and Discussion

3.1. *Suspension rheology and estimation of the particle shear modulus*

We observed that starting from $\phi \sim 0.4$, suspensions exhibit a finite value of elastic modulus. By contrast to what is observed in colloidal systems, which are liquid till the random closed packing, suspensions of granular particles can exhibit a finite modulus at volumes fractions much lower, due to the formation of a self-supporting stress-bearing network. The minimum volume fraction at which this network can form is called the random loose packing, its value depends on the shape but also the frictional properties of the particles(Silbert, 2010; Dong et al., 2006). Starting from the random loose packing, the shear modulus (measured at f = 1Hz and $\gamma = 0.01$) of dense suspensions of swollen starch granules strongly increases with volume fraction, as illustrated in figure 1. Whatever the method used to prepare dense suspensions, namely centrifugation, osmotic compression or limited water swelling, the data superimposed. Whatever the history associated with each procedure, the final stage that is reached is reproducible in terms of rheological characterization and the granule volume fraction is the key parameter that controls the elastic behaviour of the paste. Even in the case of limited water swelling, for which granule never reached their full swelling capacity due to the limited amount of water (for $\phi > 1$), the properties of the suspension are identical to the one of fully swollen starch granules that were partially dehydrated by compression. Two regimes are observed concerning the elastic modulus dependency toward volume fraction. First, from above the random loose packing to $\phi \approx 0.7$, the shear modulus strongly increases with the volume fraction. Then, a transition zone exists for $0.7 < \phi < 1$. For volume fraction $\phi > 1$, the dependence of shear modulus on volume fraction is much weaker. Insert in Figure 1 shows the log-log plot which shows the existence of the two regimes and the power law dependence of shear modulus with the notional volume fraction of granules. Fitting a power law to these regimes resulted in the following equation

$$G' = \begin{cases} 1600\phi^{3.15} & 0.4 \leq \phi \leq 0.7 \\ 550\phi^{0.53} & 1 \leq \phi \end{cases}$$

A similar increase in shear modulus with notional volume fraction have been reported by Evans and Lips (1990); Abdulmola et al. (1996); Rodriguez-Hernandez et al. (2006). The existence of two regimes of shear modulus with volume fraction for swollen starch suspensions is reported in Evans and Lips (1992). Also, for comparison Evans and Lips (1992) reported values of suspension shear modulus around 750 Pa and 1000 Pa at notional volume fraction of 1, for two different grades of chemically modified maize starches.

Whatever the volume fraction, the elastic modulus of the suspension only show a very weak dependency on the frequency. This is illustrated in the insert of figure 1 for 3 different volume fractions achieved via 3 sample preparation methods, in the first, intermediate and second regime. As reported by Seth et al. (2006), soft particle suspension moduli are function of the frequency. Seth et al. (2006) even predicted from simulations G_0 and G_∞ (storage moduli at low and high frequency). We show from the following data that the relationship of storage moduli with frequency are similar across the volume fractions tested.

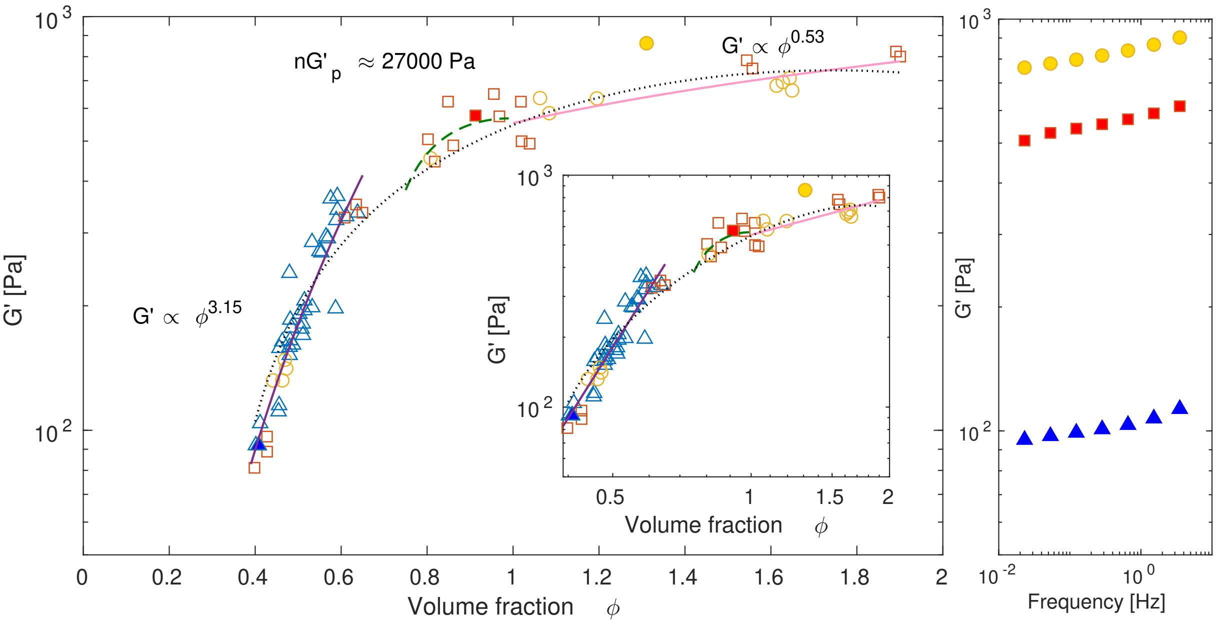

Figure 1: Suspension shear modulus as a function of volume fraction. Triangles[△], Squares[□], circles[◯] represent samples prepared via centrifugation, limited water swelling and osmotic compression respectively(γ =0.01, f = 1 Hz). The solid dotted line represents the polynomial fit of overall experimental data ($G_{suspension} = -352\phi^2 + 1229\phi - 330$). The purple continuous line represents the power-law fit for volume fractions $\phi < \phi_{rcp}$, Green dashed line represents the best fit from the Evans and Lips (1990) model for $0.8 < \phi < 1$, Pink continuous line represents the power law fit for volume fractions $\phi > 1$. *Insert*: The same figure in the log-log plot.
Right-side plot: Dependence on frequency: volume fraction of three samples prepared via centrifugation, limited water swelling and osmotic compression correspond to 0.4, 0.91, 1.31.

For friction-less systems, Evans and Lips (1990) derived an analytical equation that links the suspension shear modulus with the individual granule shear modulus and the average number of neighbouring granules. This model assumes a Hertzian potential (contact model) between granules. The equation, valid for $\phi_{rcp} < \phi < 1$, is as follows:

$$G'_{susp} = \frac{\phi_{rcp} n G'_p}{5\pi(1-\nu)} \left(\left(\frac{\phi}{\phi_{rcp}}\right)^{\frac{1}{3}} \left(1 - \left(\frac{\phi}{\phi_{rcp}}\right)^{\frac{-1}{3}}\right)^{\frac{1}{2}} - \frac{8}{3}\left(\frac{\phi}{\phi_{rcp}}\right)^{\frac{2}{3}} \left(1 - \left(\frac{\phi}{\phi_{rcp}}\right)^{\frac{-1}{3}}\right)^{\frac{3}{2}} \right) \quad (5)$$

where G'_{susp} is the suspension shear modulus, ϕ_{rcp} is the volume fraction at random close packing and n is the average number of neighbouring granules respectively.

Given a granule size distribution one can estimate the ϕ_{rcp} based on the relationship proposed by Farr and Groot (2009) as previously done in Shewan and Stokes (2015a,b); Shewan et al. (2021). In the system investigated, the size distribution of Feret diameters of swollen starch granules has been previously determined, it is characterized by a normal distribution with mean = 33.1 μm and standard deviation = 10.7 μm. With this value, ϕ_{rcp} = 0.68 was determined . The average number of neighbours for each granule, n, was estimated using confocal microscopy. This method was previously used for PMMA spheres by van der Vaart et al. (2013) and also allowed to measure the pair correlation function. In fact, they predicted suspension shear moduli at high frequency with Young's modulus obtained from atomic force microscopy and pair correlation function from confocal microscopy.

In figure 1 we show the fit of equation 5 for the truncated data in the volume fraction range of $\phi_{rcp} < \phi < 1$. As we can see from equation 5, G_p depends on the assumption of the average coordination number n of each granule. To determine n, confocal images were acquired on suspensions and the coordination number of 10 different granules was manually counted for each of them, based on the contacts that were observed in different layers.

Figure 2 shows the confocal cross-section image of the starch granule suspension at $\phi = 0.4$, the maximum fraction that could be reached for which each granule could still be easily distinguished from its neighbours. Here, $\phi < \phi_{rcp}$ and has n could depend on ϕ(van Hecke, 2009), the value determined at this volume fraction might differ from the one at $\phi = 1$, that should be used to apply the Evans and Lips model. Experimental studies have shown that once particles are in contact, further compression first result in a decrease in the void fraction de Aguiar et al. (2018) and local deformation at the contact point de Aguiar et al. (2017). As a result, the increase in coordination number with volume fraction might be limited, especially if friction is present in the system. From the image acquired by confocal microscopy, it is evident that the starch granules are far from being spherical. It should be noted that if the granule seems hollow, this is likely due to the fact that dye (congo red) is adsorbed only on the surface of the granule. In figure 2 we tracked one selected granule from its base (top-left image) to its top (bottom-right image). For this selected granule 5 contacts

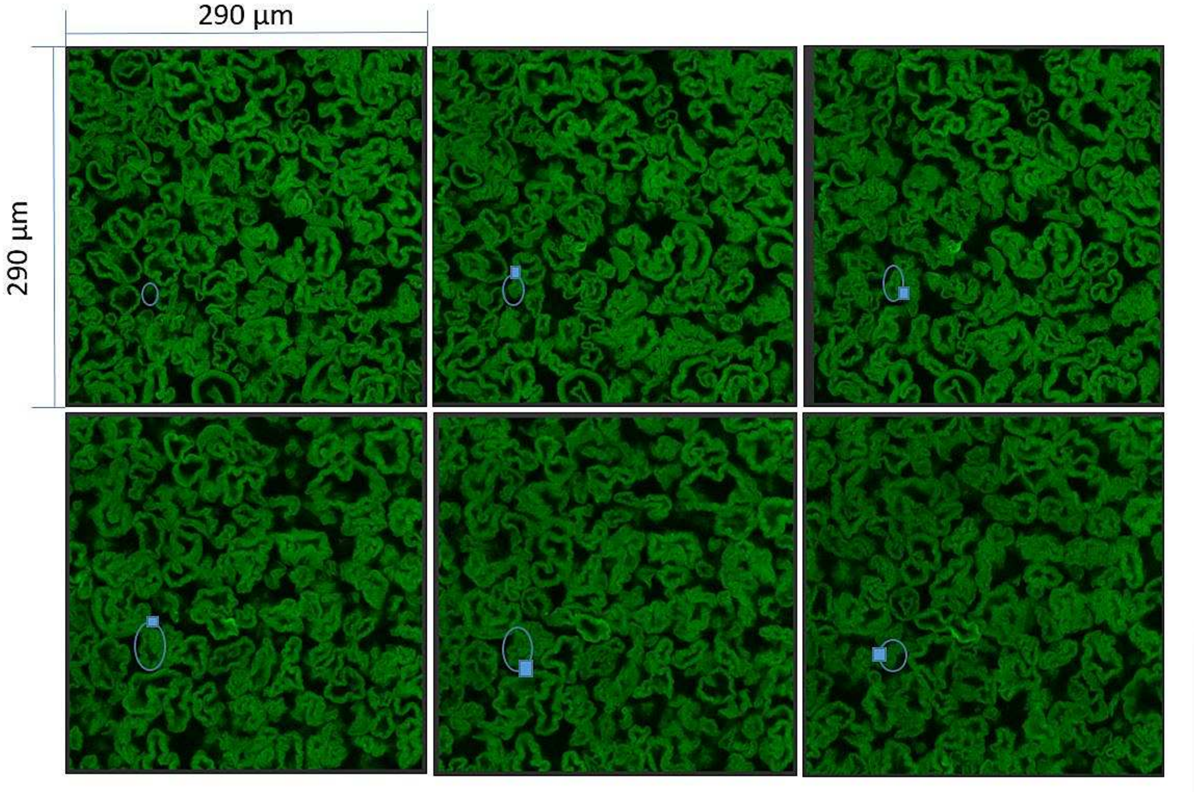

Figure 2: Confocal stack images of starch granule suspension.
Blue Boxes (□) correspond to the contact of the traced granule with the neighbouring granule.

were observed with neighbouring granules (highlighted as blue boxes on the pictures). This analysis was carried out to analyze ten different granules, for which we found coordination numbers varying from 5 (min) to 8 (max).

Therefore, with n = (5,8) and a Poisson's ratio n = 0.5, values obtained for the particle modulus were between $G_p \approx 5300$ Pa and $G_p \approx 3300$ Pa.

However, as seen in the confocal images, the particles are far from being spherical and have hair-like protrusions on the surface. This suggests that friction might be present in the system, which is coherent with the measure of a finite shear modulus at low volume fraction, the hallmark of the system above random loose packing concentration. Assuming a fully frictional case, $G_p \approx G_{suspension}$ at ϕ around 1, and we obtain $G_p \approx 550$ Pa.

3.2. Estimation of particle bulk modulus

To estimate the starch granule bulk modulus, we used osmotic compression experiments as previously done by de Aguiar et al. (2017) on model microgels. In general terms, the isotropic compressibility of material of volume V under a pressure P is measured by its bulk elastic modulus $K = -V\frac{dP}{dV}$. In this study, we do not measure directly the volume of the sample, but instead, we determined ϕ, which is directly proportional to the sample volume through the relation $\phi = n_p V_d / V$, where n_p is the particle's number in the sample, V_d is the average volume of a fully swollen starch granule in the diluted state, and V the volume of the entire suspension. The bulk modulus of a gelatinized starch paste, compressed under an osmotic pressure π, can then be written as $K = -(1/\phi)\frac{d\pi}{d(1/\phi)}$, or in a more simple way

$$K = \phi \frac{d\pi_{in}}{d\phi} \tag{6}$$

where π, ϕ are the applied osmotic pressure and the starch particle volume fraction in the suspension respectively. In our experiments, the osmotic pressure is directly linked to the PEG content in the water bath, so that osmotic pressures ranging from about 18 kPa to about 19 kPa were experimentally reached (Table 2)

PEG conc [wt %]	Osmotic pressure [kPa]	Volume fraction(ϕ) [%]
1	1.8	77
1.5	3.4	99
2	5.4	120
2.5	8.0	139
3	11.0	145
3.5	14.7	158
4	18.9	169

Table 2: Equilibrium osmotic pressure and volume fractions

Using equation 6, the estimates for bulk modulus at different volume fraction are shown in figure 3. Consistently with Nikolov et al. (2020) a linear relationship between suspension bulk modulus and volume fraction is obtained. The linear trend also agrees well with the experimental results of Liétor-Santos et al. (2011) for microgel particles comprising vinyl pyridine and divinyl benzene. Nikolov et al. (2020) showed that suspension bulk

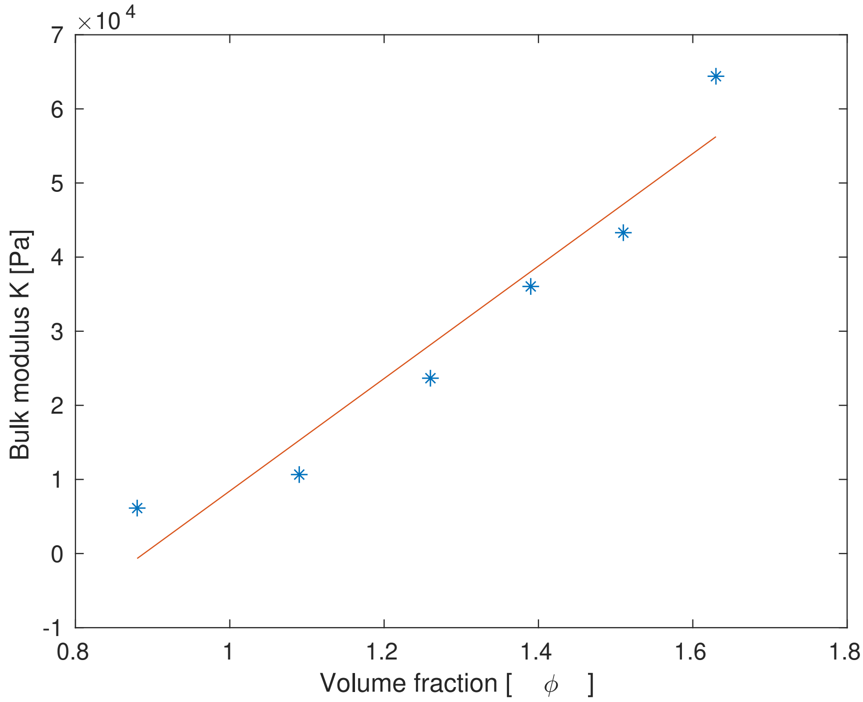

Figure 3: Suspension bulk modulus as function of volume fraction.
Asterisks[∗] correspond to experimental data.

modulus at $\phi = 1$ is roughly equal to 0.8×particle bulk modulus, and that the ratio of the suspension bulk modulus to the particle bulk modulus is independent of volume fraction for $\phi > 1$. From the linear fit in figure 3, it appears that the bulk modulus of the suspension is about 8.4 kPa at $\phi = 1$. Therefore, an estimate for our starch particle bulk modulus is $K_{particle} \approx 10.5$ kPa. Using this estimate for bulk modulus and shear modulus of the suspension at $\phi = 1$, we obtain a Poisson's ratio of 0.47, which is close to the maximum value of 0.5. By contrast, a Poisson's ratio of 0.33 is obtained if it is calculated using the friction-less spherical particle assumption. Poisson's ratio for hydrogels reported in literature ranged from 0.38 to 0.5 (Mohapatra et al., 2017; Boon and Schurtenberger, 2017). This methodology to characterize the modulus of particles is complementary to the techniques such as nano-indentation, AFM,etc (Kaufman et al., 2017; Aufderhorst-Roberts et al., 2018). Such existing alternative techniques are not straightforward to apply to measure a particle averaged modulus for such a complex system of soft particles with a very high degree of variability in terms of size and shapes.

3.3. Suspension material properties with temperature

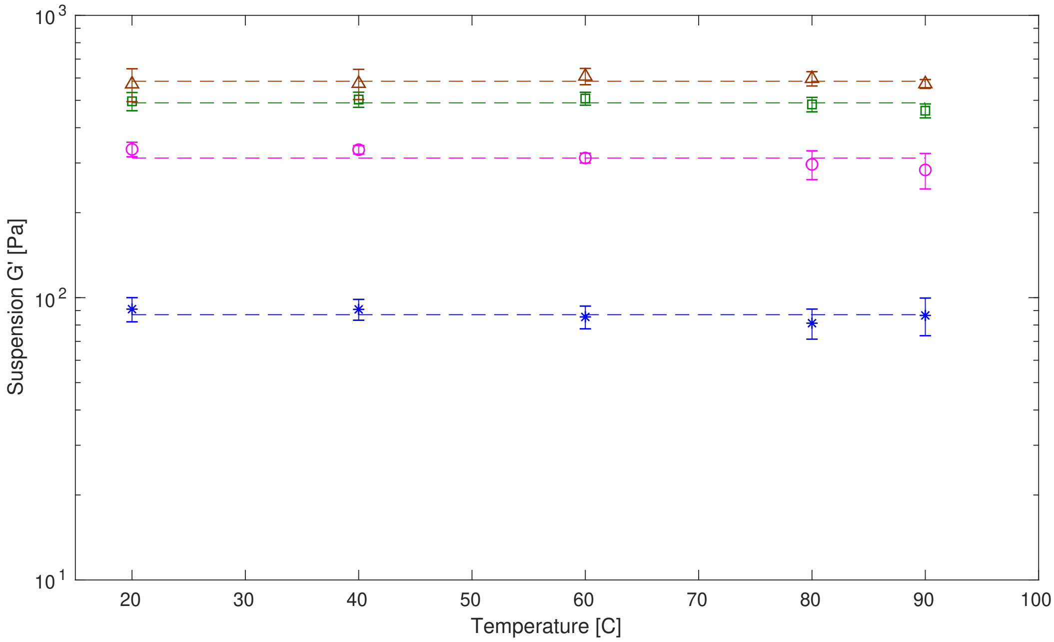

Figure 4: Storage modulus at different temperatures. Asterisks[*], circles[◯], boxes[□] and triangles[△] correspond to volume fractions ϕ of 0.42, 0.63, 0.83 and 1.03 respectively. Error bars correspond to one standard deviation. The dashed line is the mean value of all the measurements across temperatures.

The storage modulus of the suspension was measured at five different temperatures for four different volume fractions. No significant dependence of shear modulus with temperature was observed in the range of temperatures tested. In figure 4 the dotted line is the mean of the measurements of storage moduli at all temperatures for a given volume fraction. These dotted lines fall within the error bars for all volume fractions except for $\phi = 0.63$ at 40 °C. Thus, we conclude that the starch granule material properties are independent of the temperature for the tested range of 20 °C to 90 °C. Such temperature independence of hydrogels is also observed by Jing et al. (2021) for polyvinyl alcohol (PVA), carrageenan and calcium-chloride based particles as long as there is no phase change such as melting.

3.4. Conclusion

This study focused on the rheological properties of fully gelatinized chemically modified waxy maize starch. We characterized suspension shear modulus and suspension bulk modulus at different particles volume fractions, which was reached thanks to three different and independent techniques: centrifugation of a diluted suspension, osmotic compression of a diluted suspension, and controlled swelling of the granules with a limited amount of water. These different techniques allowed to reach a large range of volume fractions but also gave coherent results showing the results are not technique-dependant. The shear and bulk moduli were determined by rheometry and osmotic compression, respectively. From these macroscopic measurements, we estimated the mechanical properties of an "averaged" swollen granule. We first discussed the equation previously used by Evans and Lips (1990), which can be used to estimate the particle shear modulus from the suspension shear modulus, and required an estimate of the average number of neighbouring granules. This was roughly estimated manually using the layered scans of confocal microscopy. Besides Evans and Lips (1990) equation is only valid for perfectly spherical friction-less spheres, which is rarely the case in naturally occurring systems such as starch suspensions, this approach could give an upper bound for the particle shear modulus which was estimated to be around 4400 Pa for this starch. For the lower bound, we considered frictional interactions so that the particle shear modulus is nearly identical to the suspension shear modulus at a volume fraction close to 1. From this assumption, an estimate of particle modulus of 550 Pa was obtained. It seems reasonable, notably in view of the 'roughness' of the observed granules to consider rather the second hypothesis. Therefore, assuming frictional interactions, the bulk modulus of the particle was estimated to be around 10.5 kPa. Interestingly, the suspension shear modulus, measured at different volume fractions, were found to be independent of temperature, which strongly suggests that starch granules mechanical properties are temperature independent in the range of temperature investigated here. Finally, in a first approach, for this kind of starch, in a fully swollen state, Young's modulus and Poisson's ratio of the granules are approximately 1.8 kPa and 0.47 respectively. These estimates could find use in research using modelling and simulation techniques such as DEM and CFD-DEM which in turn help in designing process equipment, process intensification, optimization and designing model-based process control. This methodology can be applied to estimate properties of similar microgel systems and of different grades of chemically modified waxy maize starches.

4. Acknowledgments

This research has been carried out with funding from European Union as part of EU RESEARCH FRAMEWORK PROGRAMME: H2020 / Marie Skłodowska-Curie Actions ITN MATHEGRAM [813202].

References

A. R. Abate, L. Han, L. Jin, Z. Suo, and D. A. Weitz. Measuring the elastic modulus of microgels using microdrops. *Soft Matter*, 8(39):10032–10035, 2012.

N. Abdulmola, M. Hember, R. Richardson, and E. Morris. Effect of xanthan on the small-deformation rheology of crosslinked and uncrosslinked waxy maize starch. *Carbohydrate Polymers*, 31(1-2):65–78, 1996.

A. Aufderhorst-Roberts, D. Baker, R. J. Foster, O. Cayre, J. Mattsson, and S. D. Connell. Nanoscale mechanics of microgel particles. *Nanoscale*, 10(34):16050–16061, 2018.

G. Batchelor. The effect of brownian motion on the bulk stress in a suspension of spherical particles. *Journal of Fluid Mechanics*, 83(1):97–117, 1977.

N. Boon and P. Schurtenberger. Swelling of micro-hydrogels with a crosslinker gradient. *Physical Chemistry Chemical Physics*, 19(35):23740–23746, 2017.

G. Chen, O. H. Campanella, and S. Purkayastha. A dynamic model of crosslinked corn starch granules swelling during thermal processing. *Journal of Food Engineering*, 81(2):500–507, 2007.

M. Cloitre, R. Borrega, and L. Leibler. Rheological aging and rejuvenation in microgel pastes. *Physical Review Letters*, 85(22):4819, 2000.

J. Cohen, R. Podgornik, P. L. Hansen, and V. Parsegian. A phenomenological one-parameter equation of state for osmotic pressures of peg and other neutral flexible polymers in good solvents. *The Journal of Physical Chemistry B*, 113(12):3709–3714, 2009.

I. B. de Aguiar, T. Van de Laar, M. Meireles, A. Bouchoux, J. Sprakel, and K. Schroën. Deswelling and deformation of microgels in concentrated packings. *Scientific Reports*, 7(1):1–11, 2017.

I. B. de Aguiar, K. Schroën, M. Meireles, and A. Bouchoux. Compressive resistance of granular-scale microgels: From loose to dense packing. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 553:406–416, 2018.

F. Deslandes, A. Plana-Fattori, G. Almeida, G. Moulin, C. Doursat, and D. Flick. Estimation of individual starch granule swelling under hydro-thermal treatment. *Food Structure*, 22:100125, 2019.

A. Di Renzo and F. P. Di Maio. An improved integral non-linear model for the contact of particles in distinct element simulations. *Chemical engineering science*, 60(5):1303–1312, 2005.

K. Dong, R. Yang, R. Zou, and A. Yu. Role of interparticle forces in the formation of random loose packing. *Physical review letters*, 96(14):145505, 2006.

A. Einstein. *Eine neue bestimmung der moleküldimensionen.* PhD thesis, ETH Zurich, 1905.

I. Evans and A. Lips. Viscoelasticity of gelatinized starch dispersions. *Journal of Texture Studies*, 23(1): 69–86, 1992.

I. D. Evans and A. Lips. Concentration dependence of the linear elastic behaviour of model microgel dispersions. *Journal of the Chemical Society, Faraday Transactions*, 86(20):3413–3417, 1990.

R. S. Farr and R. D. Groot. Close packing density of polydisperse hard spheres. *The Journal of chemical physics*, 131(24):244104, 2009.

Y. He, Z. Wang, T. Evans, A. Yu, and R. Yang. Dem study of the mechanical strength of iron ore compacts. *International Journal of Mineral Processing*, 142:73–81, 2015.

H. Jing, J. Shi, P. Guoab, S. Guan, H. Fu, and W. Cui. Hydrogels based on physically cross-linked network with high mechanical property and recasting ability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 611:125805, 2021.

G. Kaufman, S. Mukhopadhyay, Y. Rokhlenko, S. Nejati, R. Boltyanskiy, Y. Choo, M. Loewenberg, and C. O. Osuji. Highly stiff yet elastic microcapsules incorporating cellulose nanofibrils. *Soft Matter*, 13(15): 2733–2737, 2017.

J. E. Lane, P. T. Metzger, and R. A. Wilkinson. A review of discrete element method (dem) particle shapes and size distributions for lunar soil. *NASA STI*, 2010.

J. Li, M. Turesson, C. A. Haglund, B. Cabane, and M. Skepö. Equation of state of peg/peo in good solvent. comparison between a one-parameter eos and experiments. *Polymer*, 80:205–213, 2015.

J. J. Liétor-Santos, B. Sierra-Martín, and A. Fernández-Nieves. Bulk and shear moduli of compressed microgel suspensions. *Physical Review E*, 84(6):060402, 2011.

J. Mattsson, H. M. Wyss, A. Fernandez-Nieves, K. Miyazaki, Z. Hu, D. R. Reichman, and D. A. Weitz. Soft colloids make strong glasses. *Nature*, 462(7269):83–86, 2009.

P. Menut, S. Seiffert, J. Sprakel, and D. A. Weitz. Does size matter? elasticity of compressed suspensions of colloidal-and granular-scale microgels. *Soft Matter*, 8(1):156–164, 2012.

H. Mohapatra, T. M. Kruger, T. I. Lansakara, A. V. Tivanski, and L. L. Stevens. Core and surface microgel mechanics are differentially sensitive to alternative crosslinking concentrations. *Soft matter*, 13(34):5684–5695, 2017.

H. Nawaz, R. Waheed, M. Nawaz, and D. Shahwar. Physical and chemical modifications in starch structure and reactivity. *Chemical properties of starch*, page 13, 2020.

S. V. Nikolov, A. Fernandez-Nieves, and A. Alexeev. Behavior and mechanics of dense microgel suspensions. *Proceedings of the National Academy of Sciences*, 117(44):27096–27103, 2020.

L. Orefice and J. G. Khinast. A novel framework for a rational, fully-automatised calibration routine for dem models of cohesive powders. *Powder Technology*, 361:687–703, 2020.

A. Palanisamy, F. Deslandes, M. Ramaioli, P. Menut, A. Plana-Fattori, and D. Flick. Kinetic modelling of individual starch granules swelling. *Food Structure*, page 100150, 2020.

D. S. Preece, R. P. Jensen, E. D. Perkins, J. R. Williams, et al. Sand production modeling using superquadric discrete elements and coupling of fluid flow and particle motion. In *Vail Rocks 1999, The 37th US Symposium on Rock Mechanics (USRMS)*. American Rock Mechanics Association, 1999.

W. S. Ratnayake and D. S. Jackson. Starch gelatinization. *Advances in Food and Nutrition Research*, 55: 221–268, 2008.

S. Renzetti, I. A. van den Hoek, and R. G. van der Sman. Mechanisms controlling wheat starch gelatinization and pasting behaviour in presence of sugars and sugar replacers: Role of hydrogen bonding and plasticizer molar volume. *Food Hydrocolloids*, 119:106880, 2021.

Reportlinker.com. Global starch industry. *GLOBE NEWSWIRE, New York*, 2020.

A. Rodriguez-Hernandez, S. Durand, C. Garnier, A. Tecante, and J. L. Doublier. Rheology-structure properties of waxy maize starch–gellan mixtures. *Food Hydrocolloids*, 20(8):1223–1230, 2006.

J. R. Seth, M. Cloitre, and R. T. Bonnecaze. Elastic properties of soft particle pastes. *Journal of rheology*, 50(3):353–376, 2006.

H. M. Shewan and J. R. Stokes. Analytically predicting the viscosity of hard sphere suspensions from the particle size distribution. *Journal of Non-Newtonian Fluid Mechanics*, 222:72–81, 2015a.

H. M. Shewan and J. R. Stokes. Viscosity of soft spherical micro-hydrogel suspensions. *Journal of colloid and interface science*, 442:75–81, 2015b.

H. M. Shewan, G. E. Yakubov, M. R. Bonilla, and J. R. Stokes. Viscoelasticity of non-colloidal hydrogel particle suspensions at the liquid–solid transition. *Soft Matter*, 17(19):5073–5083, 2021.

L. E. Silbert. Jamming of frictional spheres and random loose packing. *Soft Matter*, 6(13):2918–2924, 2010.

K. van der Vaart, Y. Rahmani, R. Zargar, Z. Hu, D. Bonn, and P. Schall. Rheology of concentrated soft and hard-sphere suspensions. *Journal of Rheology*, 57(4):1195–1209, 2013.

M. van Hecke. Jamming of soft particles: geometry, mechanics, scaling and isostaticity. *Journal of Physics: Condensed Matter*, 22(3):033101, 2009.

M. M. Villone and H. A. Stone. Rotating tensiometer for the measurement of the elastic modulus of deformable particles. *Physical Review Fluids*, 5(8):083606, 2020.

M. M. Villone, J. K. Nunes, Y. Li, H. A. Stone, and P. L. Maffettone. Design of a microfluidic device for the measurement of the elastic modulus of deformable particles. *Soft matter*, 15(5):880–889, 2019.

Z. Yan, S. K. Wilkinson, E. H. Stitt, and M. Marigo. Investigating mixing and segregation using discrete element modelling (dem) in the freeman ft4 rheometer. *International journal of pharmaceutics*, 513(1-2): 38–48, 2016.